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Investigation of the Composition of the Ash of Hydrocarbon Fuels

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INVESTIGATION OF THE COMPOSITION OF THE ASH OF
HYDROCARBON FUELS
[Issledovanie sostava zoly uglevodorodnykh topliv]

by

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Hydrocarbon fuels contain compounds with ash (metals and metalloids) elements—organo-metallic compounds—in very small quantities. These elements, in the form of oxides, are concentrated in the ash after combustion of the fuels. In spite of the low content of compounds with ash elements in fuels, their effect on the operational properties of the fuels is extraordinarily great [1].

Intensified gas corrosion of jet engines and gas turbine units is observed in the presence of compounds with ash elements. An increase in the content of organo-metallic compounds and other compounds with ash elements in motor-engine fuels entails an increase

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Table 1

Physical and chemical properties of initial fuels

Показатели /	2 T-2	3 TC-1		4 T-1	5 DA
		до гидро- очистки	после гид- роочистки		
9 Плотность ρ_4^{20} , г/см ³	0,7701	0,7762	0,7760	0,8197	0,8491
9 Пределы выпаривания, °C	73-248	140-240	138-230	141-280	181-328
10 Молекулярный вес	136,0	140,6	140,2	148,0	174,0
11 Содержание фактических смол, мг/100 мл	2,2	2,4	0,5	5,4	6,4
12 Содержание ароматических углеводо- родов, % вес.	15,0	15,7	15,6	16,3	20,1
13 Содержание серы, % вес.	0,120	0,156	0,011	0,057	0,136
14 Содержание меркаптановой серы, % вес.	0,003	0,0072	0,0002	0,005	0,022
15 Зольность, %	0,003	0,004	0,002	0,006	0,008
16 Месторождение нефти	Муханов- ское /8	Туймазинское /9		Бакпийский район /20	

Key: 1-Indicators

2-T-2

3-TS-1

4-T-1

5-DA

6-before hydro-
refining7-after hydro-
refining8-Density ρ_4^{20} ,
g/cm³9-Limits of evapo-
ration by boiling

10-Molecular weight

11-Content of actual
resins, mg/100 ml

12-Content of aromatic

hydrocarbons, % weight

13-Content of sulphur, % weight

14-Content of mercaptan sulphur,
% weight

15-Ash content, %

16-Place of origin of crude
oil

17-Absent

18-Mukhanovskii

19-Tuymazinskii

20-Bakinskii rayon

in the amount of carbon deposits in the combustion chamber of piston engines [2]. In addition, it has been established that compounds with ash elements promote the formation of insoluble sludge and resins during heating of the fuels [1-3].

The purpose of the present study is the investigation of the composition of the ash of fuels T-2, TS-1, T-1, and DA.

Commercial fuels, the characteristics of which are given in

table 1, were used for the investigation.

Fuels TS-1 and T-1 are widely used in civil aviation jets [4]. Fuel DA is used in high-speed engines with compression ignition under arctic conditions.

For obtaining the ash, 20 liters of fuel were distilled in a flask, and the residue from the flask was evaporated in a porcelain bowl to a dry residue, which was baked in a muffle furnace at a temperature of 450°C.

The composition of the ash was determined on a "Hilger" spectrograph. The obtained spectrograms were interpreted on a spectrum projector using an atlas of spectral lines and tables. Analysis of the composition of the ash was carried out on 41 elements¹. The results of the analysis are given in table 2.

It ought to be noted that the ash of fuels T-1 and DA, obtained from crude oil of the Bakinskii region, contains more silicon, iron, copper, and zinc than sulphur fuels. The ash of the Bakinskii fuels contains a greater amount of lead and sodium. In fuels T-2 and TS-1, much vanadium and nickel is present, and sufficiently large amounts of zinc, silicon, and calcium were detected.

As a result of hydrotreating of fuel TS-1 in an aluminocobalt-molybdenum catalyst, the content of magnesium, nickel, copper, and arsenic decreased, and vanadium, titanium, antimony, and sodium were removed, but the amount of aluminum, chromium, and barium increased. Molybdenum also appeared in the composition of the ash.

¹Ye. Ya. Smirnova took part in the implementation of the experimental portion of the study.

Table 2

Composition of the ash of the investigated fuels

Элементы	2 T-2	3 ТС-1		4 T-1	5 ДА
		до гидро- очистки (товарное)	после гидро- очистки		
Зольность, %	0,003	0,004	0,002	0,006	0,008
Металлы и металлоиды					
в золе, %:					
10 кремний	13-16	13-16	13-16	>18	>18
11 алюминий	0,03	0,3	0,5-1,0	0,7-2,0	0,8-1,0
12 магний	1,0	~3,0	0,5-1,0	~3,0	0,03-0,10
13 кальций	5,0	3,0-5,0	1,1-5,0	1-3	3-4
14 железо	3,0-5,0	1,0-3,0	1,0-3,0	6,0-8,0	8,0-10,0
15 марганец	0,006	0,03	0,05-0,1	0,3-1,0	0,01
16 никель	>12	>12	0,03	0,3-1,0	0,3-1,0
17 титан	0,05	0,05	Отсутствует	0,1	0,3
18 ванадий	>15,0	>15,0	Отсутствует	Отсутствует	Отсутствует
19 хром	Отсутствует	0,05	0,1-0,3	0,1-0,3	0,1-0,3
20 молибден	Отсутствует	Отсутствует	0,05-0,1	Отсутствует	Отсутствует
21 медь	3-6	5-10	3-6	>20,0	>20,0
22 свинец	0,01-0,03	0,1-0,3	0,01-0,03	0,3-1,0	0,3-1,0
23 серебро	0,03	0,03	0,01	0,03	0,05
24 сурьма	0,01	0,01	Отсутствует	0,01	0,01
25 мышьяк	0,6	0,1-0,3	0,05	Отсутствует	Отсутствует
26 цинк	2-3	3-8	2-3	15,0	15,0
27 кадмий	0,1-0,2	0,3-1,0	0,2-0,3	0,3-1,0	0,1-0,3
28 олово	0,3	0,3	0,2-0,5	0,1-0,3	0,3
29 барий	0,05	0,03	0,01	0,1-0,3	0,3
30 натрий	0,01	0,01	Отсутствует	0,3-1,0	0,3-1,0

Note. Cobalt, tungsten, zirconium, hafnium, niobium, tantalum, bismuth, tellurium, thallium, germanium, gallium, indium, yttrium, lanthanum, strontium, lithium, phosphorous, scandium, beryllium are absent in the ash.

Key: 1-Elements

2-T-1

3-TS-1

4-T-1

5-DA

6-before hydrotrefining

7-after hydrotrefining

8-Ash content, %

9-Metals and metalloids

10-silicon

11-aluminum

12-magnesium

13-calcium

14-iron

15-manganese

16-nickel

17-titanium

18-vanadium

19-chromium

20-molybdenum

21-copper

22-lead

23-silver

24-antimony

25-arsenic

26-zinc

27-cadmium

28-tin

29-barium

30-sodium

31-Absent (appears 13 times in table)

Practically those same elements are present in the ash of crude oils (table 3) as in the fuels obtained from them, but in

relatively larger quantities (by 10-20 times). The ratio of the elements in the initial crude oils and in the fuels is, on the whole, maintained; however, one ought to note that strontium and cobalt, which are not detected in the fuels, are present in the initial crude oils.

Evidently, metals are in the crude oil as organo-metallic compounds and complexes (vanadium, nickel, iron, aluminum, zinc, etc.). Their origin is not precisely known. Some researchers consider them primary products, and some, secondary products [5].

At present, it is considered almost a proven fact that organic vanadium compounds are concentrated in the resinous portion of crude oil, and organic nickel in the oil portion [5]. However, a certain portion of the compounds with ash elements enters the medium-distillate fractions of the crude oil during refining (see tables 2 and 3).

The ash elements in the fuel can enter from the initial crude oil during its refining, as a result of their contact with the construction materials of various equipment, and from the air together with dust during storage, transporting, and use of the fuels in vehicles. This is supported by the results of research on the composition of the ash of the initial fuels, having been stored for four years in hermetically sealed iron tanks, in glass bottles, and in glass bottles with copper plates (table 4). For the purpose of elucidating the effect of ordinary (unpurified) atmospheric air on the composition of the ash and on the increase in the total ash content of the fuels, the composition of fuel

TS-1, through which atmospheric air in a 1000-fold volume was passed, was also investigated. The process of introducing dust into the fuel was artificially intensified. The schematic of

Table 3

Composition of the ash of the initial crude oils

Элементы	Туймазин- ская	Мухомовская	Бакинская
5 Зольность, %	0,04	0,06	0,08
6 Металлы и металлоиды в золе, %:			
7 кремний	12,0-15,0	15,0	~20
8 алюминий	5,0	6,0	~1,0
9 магний	~3,0	~3,0	>3,0
10 кальций	5,0	8,0	>4,0
11 железо	~8,0	~8,0	13,0
12 марганец	0,1	0,4	0,6
13 никель	>15,0	>15,0	~2,0
14 титан	0,05	0,01	0,06
15 ванадий	>18,0	>20,0	~0,01
16 хром	~0,6	~0,6	~1,0
17 медь	>10,0	>10,0	~20,0
18 свинец	0,03	0,01	~1,0
19 серебро	0,6	0,3	0,1
20 сурьма	0,001	0,01	0,03
21 мышьяк	0,09	0,1	Отсутствует
22 цинк	~10,0	~9,0	~20,0
23 кадмий	0,1	0,1	1,0
24 олово	0,1	0,6	0,5
25 барий	0,08	0,15	>0,1
26 натрий	~0,1	~0,2	>3,0
27 стронций	0,1	0,4	1,0
28 кобальт	Отсутствует	Отсутствует	0,02

Note. Tungsten, zirconium, hafnium, niobium, tantalum, bismuth, tellurium, thallium, germanium, gallium, indium, yttrium, lanthanum, lithium, phosphorous, scandium, and beryllium are absent in the ash.

Key: 1-Elements	15-vanadium
2-Tuymazinskii	16-chromium
3-Mukhanovskii	17-copper
4-Bakinskii	18-lead
5-Ash content, %	19-silver
6-Metals and metalloids in ash, %	20-antimony
7-silicon	21-arsenic
8-aluminum	22-zinc
9-magnesium	23-cadmium
10-calcium	24-tin
11-iron	25-barium
12-manganese	26-sodium
13-nickel	27-strontium
14-titanium	28-cobalt
	29-Absent (occurs 3 times in table)

the instrument for the artificial increase of the ash content of the fuels is shown in figure 1.

As is evident from the given data, after four-year storage in iron tanks, the ash content of the fuel increased by 1.5 times; in the ash, the iron content increased (fig. 2). With storage of the fuel in glass bottles in the presence of copper, the ash content of the fuel increased by more than 2 times, and the

Table 4

Composition of the ash of TS-1 fuel after prolonged storage and artificial increasing of the ash content in it

1 Элементы	2 Хранение			4 После искус- ственного введения пыли из атмосферы
	3 в железных бочках	4 в стеклян- ных бутылках	5 в стеклян- ных бутылках с медными пластинками	
7 Золистость, %	0,000	0,004	0,009	0,018
8 Элементы в составе золы, %:				
9 кремний	13-15	13-15	13-15	~40
10 алюминий	~1,0	~1,0	~1,0	~3,0
11 магний	1,0	1,0	1,0	~1,5
12 железо	~20,0	1,0-3,0	1,0-3,0	~5,0
13 медь	3-6	3-6	~22,0	3-6
14 кальций	~5,0	~5,0	~5,0	~8,0
15 цинк	3,8	3,8	3,8	~10,0

Key: 1-Elements
 2-Storage
 3-in iron tanks
 4-in glass bottles
 5-in glass bottles
 with copper plates
 6-After artificial
 introduction of
 dust from the air
 into the fuel
 8-Elements in the ash
 composition, %
 9-silicon
 10-aluminum
 11-magnesium
 12-iron
 13-copper
 14-calcium
 15-zinc

copper content also increased considerably. The ash content of the fuel and the composition of the ash was practically unchanged with storage in glass bottles (without copper).

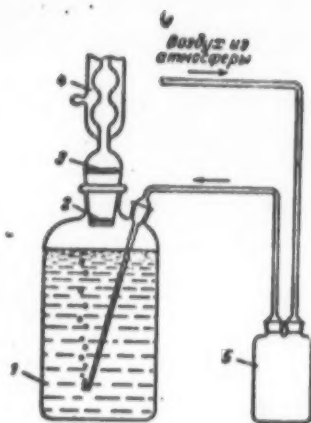


Fig. 1. Principle diagram of instrument for the artificial introduction of dust into the fuel:

1-vessel with fuel; 2,3-drop traps; 4-reflux condensor; 5-buffer vessel; 6-air from atmosphere.

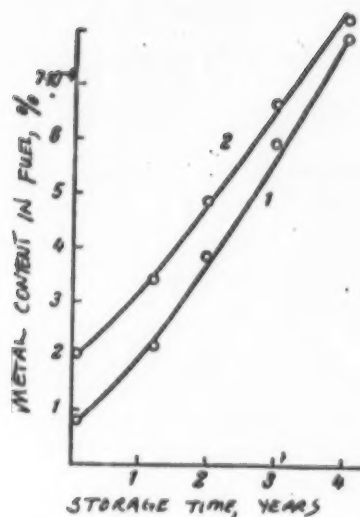


Fig. 2. Increase in the content of iron and copper in fuel TS-1 with storage:

1-in iron tanks; 2-in glass bottles with copper plates.

After the artificial introduction of dust into the fuel, the content of silicon, aluminum, magnesium, calcium, and zinc in the ash increased. These elements are evidently present as inorganic compounds in the atmosphere. The total ash content of the fuel increased by 4.5 times.

There is almost always the possibility of the entry of dust into the fuels. This can occur during delivery and receiving of the fuel in warehouses, during fueling of vehicles and aircraft, or during "small" and "large" respiration of the storage tanks.

And it is not by accident that many of these elements are detected in the composition of the microimpurities which accumulate in the fuels [1].

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